

UNIT 3

THERMOCHEMISTRY |

Structure

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3.1 INTRODUCTION

In the previous units of this course you have learnt about the meaning and the importance of thermodynamics and its basic aspects. You have also learnt about the Zeroth and first law of thermodynamics and applications of the first law of thermodynamics to gaseous systems. In this unit, we would extend the application of the first law of thermodynamics and take up the study of the heat changes associated with chemical reactions. Such a study forms an important branch of thermodynamics and is called thermochemistry.

We would begin the unit by discussing the measurement of energy changes accompanying chemical reactions under the conditions of constant volume

and constant pressure. We would also introduce the concept of thermochemical equations and discuss its significance. We would then introduce the concept of standard enthalpy changes and argue for the need for a standard state and define it. This will be followed by a discussion on the enthalpy changes accompanying chemical reactions. Herein we would introduce the concept of standard enthalpy of formation and discuss about its direct and indirect determination.

Since temperature is one of the important variables in thermodynamics; we would also be taking up the variation in the enthalpy changes with temperature. In this context we shall derive Kirchhoff's equation and discuss its importance. Towards the end of the unit we would introduce the concept of bond enthalpy and demonstrate how the bond enthalpies can be used to predict enthalpy of reaction.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define thermochemistry and discuss the energy changes accompanying chemical reactions;
- ❖ describe the methods for experimental determination of energy changes accompanying chemical reactions under constant volume and constant pressure conditions;
- ❖ explain the significance of Δ_rU and Δ_rH ;
- ❖ derive the relationship between Δ_rU and Δ_rH and solve problems based on it;
- ❖ define the standard enthalpy of formation of substances and describe a method for their direct determination;
- ❖ enlist the standard states for reactants and products in different physical states;
- ❖ state Hess' law of constant heat summation and explain its significance;
- ❖ calculate the enthalpy of different reactions using enthalpies of formation of reactants and products;
- ❖ define enthalpy of combustion and use enthalpy of combustion values to determine the standard enthalpy of formation of compounds;
- ❖ explain the effect of temperature on the enthalpy of a reaction and derive the Kirchhoff's equation;
- ❖ compute the enthalpy of reaction at a given temperature from that available at some other temperature;
- ❖ define and explain the meaning of bond enthalpy; and
- ❖ predict the enthalpies of reactions from bond enthalpy data.

3.2 ENERGY CHANGES ACCOMPANYING CHEMICAL REACTIONS

A chemical reaction can be seen as a process in which some of the chemical bonds of the reactants are broken and newer chemical bonds are formed in the products of the reaction. Such a process is expected to be associated with some kind of change in the chemical energy of the system. This change in chemical energy of the system may appear as heat or work or both in the surroundings. Here, we are concerned with the energy changes appearing in terms of heat. If the change in energy of the system appears as heat in the surroundings, the reaction is termed as **exothermic reaction**. For example, if we take some quick lime (CaO) and add it to water at room temperature, a chemical reaction would occur and the reaction mixture will become hot due to the heat released by the reaction. Since the energy as heat is given by the system; it would have a negative sign ($q_{\text{rxn.}} < 0$).

The chemical energy of a chemical system is the energy associated with the chemical bonds of the reactants and the intermolecular attractions between different species.

On the other hand if the chemical reaction is accompanied by absorbing heat from the surroundings, the reaction is termed **endothermic reaction**. For example, if we take some ammonium chloride (NH_4Cl) and put it in some water at room temperature, the mixture would become cold. The sign for the heat change would be positive ($q_{\text{rxn.}} > 0$). Let us see how do we measure these heat changes?

3.2.1 Measuring Heat Changes Accompanying Chemical Reactions: Calorimetry

The heat changes accompanying the chemical reactions are measured by observing the change in the temperature of its surroundings. These temperature changes along with the heat capacities of the surroundings provide the amount of heat change accompanying the reaction. The technique used for their measurement is called **calorimetry** and the reaction vessel in which the reaction is performed is referred to as a **calorimeter**. You are aware that a chemical reaction can be performed under two conditions, viz., under constant volume conditions or under constant pressure conditions. Let's first learn about heat changes under constant volume conditions. A reaction under constant volume conditions is performed in a closed vessel called **bomb calorimeter**.

Measuring Heat Changes under Constant Volume Conditions

Let us take the example of the combustion of an organic compound to learn about measuring heat changes with bomb calorimeter, Fig. 3.1. A bomb calorimeter consists of a double-walled container in which the reaction vessel (called bomb) is immersed in known quantity of water. The container is insulated from the surroundings and is fitted with a thermometer, a stirrer and an ignition system. The bomb is a steel container that contains a known quantity of the reactant and oxygen gas (also a reactant) under pressure. An electrical ignition starts the combustion (reaction with oxygen) of the organic compound. The reaction of the compound with excess of oxygen causes a minor explosion in the vessel that is why the reaction vessel is called a **bomb**.

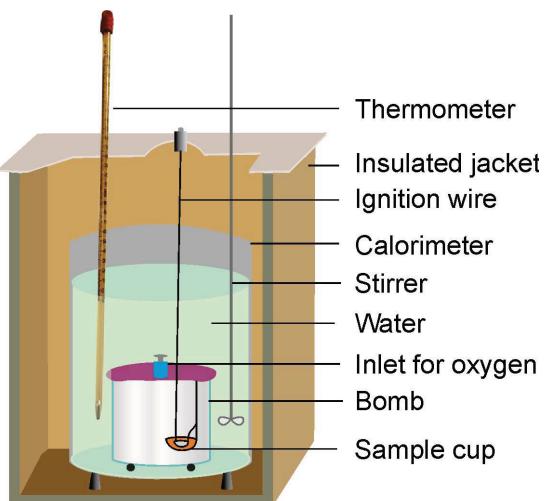


Fig. 3.1: A Bomb Calorimeter

In combustion reaction, there is an increase in the temperature of the surroundings; for some other reactions there may be a decrease in the temperature.

The heat liberated in the process is lost to the surrounding water and the calorimeter assembly causing their temperature to increase. In other words, the energy released by the combustion reaction in the form of heat is absorbed by the calorimeter and its contents. The calorimeter is so designed that no heat or mass is lost to the surroundings or we can say that the system (calorimeter with all the contents) is an isolated system. The increase in temperature due to the reaction is measured with the help of a sensitive thermometer. The increase in temperature along with the heat capacity of the calorimeter (including the bomb and the water) provides the amount of heat liberated during the reaction. Let us see how do we determine it?

In calorimetry, we need to ensure that in order to make a proper measurement of the heat change accompanying a chemical reaction we should ensure that the initial state (the reactants) and the final states (the products) of the system must have the same temperature.

As the calorimeter assembly is an isolated system, we can write,

$$q_{\text{calorimeter}} = - q_{\text{rexn.}} \quad \dots(3.1)$$

You would recall Eq. (2.21) from Unit 2

$$q_v = C \Delta T$$

for the calorimeter we can write,

$$q_{\text{calorimeter}} = C_{\text{calorimeter}} \Delta T \quad \dots(3.2)$$

The heat capacity of the calorimeter ($C_{\text{calorimeter}}$) is defined as the quantity of heat required for raising the temperature of the calorimeter assembly and its contents by one degree Celsius. The temperature change (ΔT) can be measured with the thermometer but we need to know the heat capacity of the calorimeter to determine $q_{\text{calorimeter}}$ and hence $q_{\text{rexn.}}$ The heat capacity of the calorimeter is determined in a separate experiment in which we take the same amount of water, the same bomb and use a known amount of a compound for which the heat change associated with combustion is known. Let's us take an example to understand the measurement of heat change under constant volume conditions.

Example 3.1: Combustion of 0.479 g of graphite with an excess of oxygen in a bomb calorimeter raised the temperature of the calorimeter from 298.09 K to 299.11 K. In a separate experiment, with the same

calorimeter assembly under similar conditions, the combustion of 0.50 g of benzoic acid that released 13.21 kJ of heat caused the temperature of the calorimeter to increase by 0.86 K. Calculate the heat change associated with the combustion of graphite.

Solution: As per the Eq. (3.1) and (3.2) we can write,

$$q_{\text{rxn.}} = -q_{\text{calorimeter}} = -C_{\text{calorimeter}} \Delta T$$

The ΔT is given as $299.11\text{K} - 298.09\text{K} = 1.02\text{K}$

We need to find the value of $C_{\text{calorimeter}}$. For this we make use of the given data on the combustion of benzoic acid.

We know that the heat capacity = $C = q_{\text{rxn.}} / \Delta T$

We are given, $q_{\text{rxn.}} = 13.21\text{ kJ}$ and $\Delta T = 0.86\text{ K}$

$$\text{Substituting the values, } C_{\text{calorimeter}} = \frac{13.21\text{ kJ}}{0.86\text{ K}} = 15.36\text{ kJ K}^{-1}$$

The value of $q_{\text{rxn.}}$ for combustion of graphite can be obtained by substituting the value of $C_{\text{calorimeter}}$ in the following equation,

$$q_{\text{rxn.}} = -C_{\text{calorimeter}} \Delta T$$

$$q_{\text{rxn.}} = -15.36\text{ kJ K}^{-1} \times 1.02\text{ K} = -15.68\text{ kJ}$$

Thus, the combustion of 0.479 g of graphite with an excess of oxygen is associated with the release (as the sign. Is negative) of 15.68 kJ of energy as heat.

Let us now learn about how to measure the heat changes under constant pressure conditions.

Measuring Heat Changes under Constant Pressure Conditions

In order to measure the heat changes under constant pressure conditions, in one of very simple methods, the reaction is performed in a calorimeter made from an insulating Styrofoam cup or in a thermos flask. In this set up the calorimeter is provided with a stirrer and a thermometer. The reactants are mixed in the calorimeter and the temperature changes accompanying the reaction are measured with the help of the thermometer. The insulation insures that there is no significant exchange of the heat energy with the surroundings.

The calorimeter and its contents (the reactants and the products) can be considered as an isolated system. As in the case of bomb calorimeter, here again we can write

$$q_{\text{calorimeter}} = -q_{\text{rxn.}} \quad \dots(3.1)$$

Let us take the example of neutralisation reaction between sodium hydroxide and hydrochloric acid to understand the determination of heat changes under constant pressure conditions. In a typical determination we take equal

volumes of solutions of two reactants having same concentration and mix them in the calorimeter.

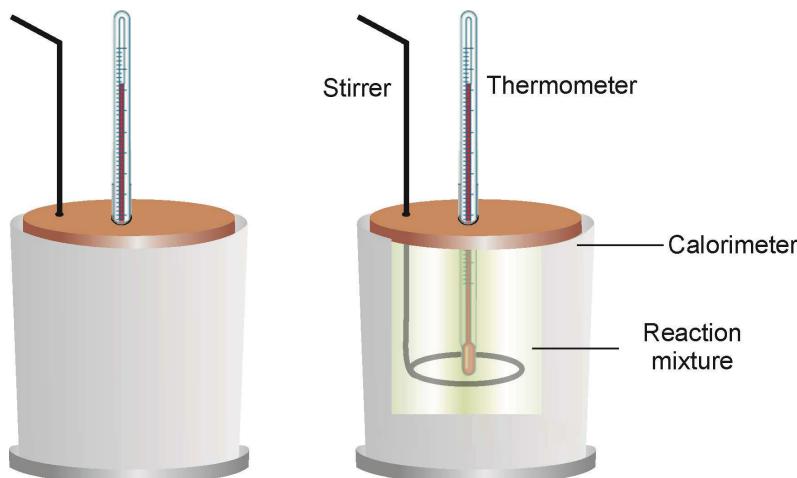


Fig. 3.2: A styrofoam calorimeter used for measuring heat change accompanying a reaction occurring at constant pressure.

The energy released in the reaction warms up the contents of the reaction mixture and the calorimeter. This fact, along with the masses, temperatures and the heat capacities of the products and the heat capacity of the calorimeter are used to determine the amount of energy released. You would actually be doing such measurements in the laboratory course BCHCL-134.

You have so far learnt about the heat changes accompanying a chemical reaction and the way to measure them under the constant volume or constant pressure conditions. We would now relate these changes with the enthalpy of reaction. However, before that why don't you answer the following simple question to assess your learning?

SAQ 1

1.75 g of ethanol (C_2H_5OH) was burned in a constant-volume bomb calorimeter and the temperature of the calorimeter assembly increased by $3.9\text{ }^{\circ}\text{C}$. If the heat capacity of the calorimeter assembly was 9.4 kJ K^{-1} , calculate the molar enthalpy of combustion of ethanol

3.2.2 Enthalpy of Reaction

Majority of chemical reactions are performed under the conditions of constant pressure, so the measured heat changes refer to the enthalpy change for the reaction. Such an enthalpy change associated with a given chemical reaction is termed as the **enthalpy of reaction**. It is denoted as Δ_rH , where r signifies the reaction and Δ , as always refers to the change in the physical quantity (final value-initial value). The question arises is that when we measure the Δ_rH values in terms of the heat changes associated with the chemical reactions what do these imply? Let us try to answer this.

In a simplified way, a chemical reaction can be represented as a process wherein the reactants get converted into the products

Here, the reactants and products respectively represent the initial state and the final state of the system. As per our understanding of the change in enthalpy ($\Delta H = H_f - H_i$) of a system we can write,

$$\Delta H = H_{\text{Products}} - H_{\text{Reactants}} \quad \dots(3.3)$$

As we know that generally we do not deal with a single reactant giving a single product; most of the times we have more species on either side of the chemical equation representing the reaction. Therefore, the enthalpy of the initial and the final state are the sum of the enthalpies of the reactants started with and the products obtained respectively. Thus,

$$\Delta_r H = (\text{sum of the } H_{\text{products}} - \text{sum of the } H_{\text{reactants}}) \quad \dots(3.4)$$

Mathematically,

$$\Delta_r H = \sum_j a_j H_m(\text{products}) - \sum_i a_i H_m(\text{reactants}) \quad \dots(3.5)$$

where, a_i 's and a_j 's are the stoichiometric coefficients for the reactants and the products respectively in the balanced chemical equation. For the reaction,



the enthalpy change can be represented as

$$\Delta_r H = 2H_m(\text{CO}_2(\text{g})) - (2H_m(\text{CO(g)}) + H_m(\text{O}_2(\text{g}))) \quad \dots(3.7)$$

Two questions arise here,

- Can we predict the enthalpy of a reaction?
- Can we calculate the enthalpies of the reactants and products from the measured value of enthalpy of reaction?

We shall take up these questions later in the unit. Let's first learn about thermochemical equations.

3.2.3 Thermochemical Equations

You are familiar with chemical equations as the symbolic representation of a given reaction that consists of the chemical formulae of the reactants and the products along with their stoichiometric coefficients. In addition, the physical state of the reactants and the products and the reaction conditions are also generally indicated. In the thermochemical equations we include the associated energy changes along with all these. For example, the thermochemical equation for the combustion of methane to give carbon dioxide and water-an exothermic process would be represented as,



A thermochemical equation can be seen as a combination of the chemical equation and the associated enthalpy change.

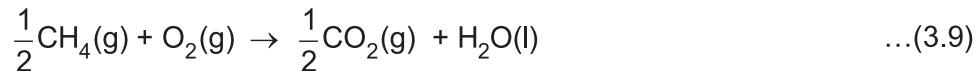
The thermochemical equation has a specific meaning and we need to understand important points about it. These are explained below.

- i) The chemical part of the equation shows that one mole of methane gas reacts with two moles of oxygen gas to give one mole of carbon dioxide

gas and two moles of liquid water. We need to understand what does the energy part convey?

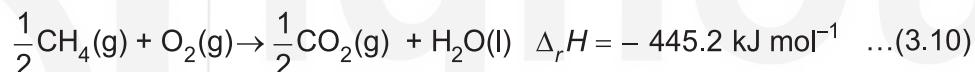
The minus sign in the energy part indicates that the reaction is exothermic, i.e., the reaction is accompanied by the release of 890.4 kJ of energy as heat to the surroundings per mole of the reaction. When we say per mole of the reaction we mean ‘the reaction as written’, i.e., in this case combustion of one mole of methane to give one mole of gaseous carbon dioxide and two moles of liquid water, releases 890.4 kJ of energy to the surroundings as heat.

As you know, the combustion of methane can also be represented by the following chemical equation.

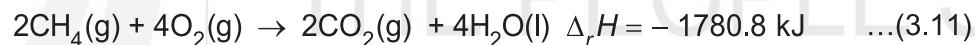


If a substance can exist in different allotropic forms, the particular form used as reactant or formed, as product must be mentioned.

What would be the enthalpy for the combustion of methane as given by Eq. (3.9)? Will it be 890.4 kJ? Our common sense tells us that if half a mole (8 g) of methane undergoes combustion it will not give as much heat as is obtained in the combustion of 1 mole (16 g) of methane; it will be half of 890.4 kJ i.e., 445.2 kJ. Therefore, the thermochemical equation for the combustion of methane as per Eq. (3.9) would be



Similarly we can argue and say that the thermochemical equation for combustion of 2 moles (32 g) of methane would be



We can generalise this fact and state that *if a thermochemical equation is multiplied by a factor ‘n’ on both sides, then the enthalpy change, $\Delta_r H$, for the reaction must also change by the same factor.*

- ii) Another important aspect of thermochemical equations is that *it is mandatory to specify the state of the reactants and the products*. Let us understand why?

We once again take the example of combustion of methane but represent it as per the following chemical equation.



What will be the enthalpy change for this reaction? Will it be 890.4 kJ? A little focus on the two equations, Eq. (3.8) and (3.12) would reveal that the products in the two equations are not same. According to the Eq. (3.8) the combustion of methane gives liquid water as one of the products whereas water is obtained in gaseous form as per Eq. (3.12). A little thinking reveals that a part of energy released in the combustion Eq. (3.12) would be used for the vaporization of 2 moles of water and accordingly the energy released, as heat in this reaction would be lesser than that obtained in Eq. (3.8). That is, the ΔH value would be lesser negative. In

fact the enthalpy change for the combustion of methane as per Eq. (3.12) has been found to be $-802.4 \text{ kJ mol}^{-1}$.

- iii) Third important feature of the thermochemical equations is that *if we reverse the equation, i.e., we refer to the reaction where the products react to give reactants, then the sign of enthalpy change would reverse; magnitude remaining the same*. Let us take the following thermochemical equation,



The thermochemical equation for the reverse reaction would be



The justification for this feature lies in the fact that the enthalpy is a state function.

3.2.4 Standard Enthalpy Change for a Reaction, $\Delta_r H^\circ$

We have seen above that the enthalpy change for a reaction depends on the physical state of the reactants used and the products formed. In addition, the enthalpy change of a reaction is also found to depend on other factors also. Therefore, in order to report unambiguous and unique value for the enthalpy change for a reaction, it becomes necessary to specify the following parameters while reporting enthalpy values.

- The physical state (solid, liquid or gas, the proper allotropic form for the solid, if applicable) of the reactants and products
- Pressure
- Temperature
- Concentration (for reactions in solution)

The specification of the parameters listed above makes the data on enthalpy change more reliable, but we may still have problem if we compare the data at different temperatures and /or pressures etc. Therefore, a new parameter called **standard enthalpy change** has been defined. *The standard enthalpy change is defined as the enthalpy change for a reaction in which the reactants and products are in their standard states and is denoted as, $\Delta_r H^\circ$.* This raises the need to define a standard state. The standard states for reactants or products in different physical states are defined as:

- The standard state of a solid substance is the pure crystalline substance, at a pressure of 1 bar and temperature of interest. For example, standard state of carbon at 298.15 K is graphite, and for tin it is the white form.
- The standard state of a liquid substance is the pure liquid substance, at a pressure of 1 bar and temperature of interest. For example, the standard state of mercury is liquid mercury at 298.15 K.

This aspect of thermochemical equation is based on an important law of thermochemistry proposed by A. L. Lavoisier and P. S. Laplace (1780). The law follows directly from the First Law of thermodynamics and states that, “the quantity of heat which must be supplied to decompose a compound into its elements is equal to the heat evolved when the compound is formed from its elements”. This can be generalised as, “the heat change accompanying a chemical reaction in one direction is exactly equal in magnitude, but opposite in sign, to that associated with the same reaction in the reverse direction”.

The standard state of a substance at a specified temperature is its pure form at a pressure of 1 bar.

For phosphorus the standard state is defined to be white phosphorus as against the most stable red allotrope. The choice is based on the fact that the white phosphorous is the more reproducible form at 298.15 K.

- The standard state of a gaseous substance is the ideal gas (hypothetical) at a pressure of 1 bar and temperature of interest. For example, the reference state of nitrogen is N₂ gas at 298.15 K. Similarly, for oxygen as an element the molecular oxygen (O₂) - the more stable form at 298.15 K, than the allotropic form, ozone (O₃) is the standard state.

Though the definition of standard state is at the temperature of interest, usually the data is taken at 298.15 K.

3.2.5 Relationship between Δ_rU and Δ_rH

You have learnt that the energy changes accompanying a chemical reaction can be measured under constant volume (in a bomb calorimeter) or under constant pressure conditions. These are equal respectively to the Δ_rU and Δ_rH for the reaction. Let us try to establish a relationship between them. For a generalised chemical reaction,



Let the thermodynamic parameters for the initial state (reactants) and the final state (products) be as follows

Initial state
(p_1, V_1, U_1, H_1)

Final state
(p_2, V_2, U_2, H_2)

According to Eq. (2.32), we can write,

$$H_1 = U_1 + p_1V_1 \quad \text{and} \quad H_2 = U_2 + p_2V_2$$

The expression for the enthalpy change for the reaction would be,

$$\Delta_rH = H_2 - H_1 = (U_2 + p_2V_2) - (U_1 + p_1V_1) \quad \dots(3.16)$$

$$= (U_2 - U_1) + (p_2V_2 - p_1V_1)$$

$$\Rightarrow \Delta_rH = \Delta_rU + (p_2V_2 - p_1V_1) \quad \dots(3.17)$$

Under the conditions of constant pressure ($p_1 = p_2 = p$),

$$\Rightarrow \Delta_rH = \Delta_rU + (pV_2 - pV_1) = \Delta_rU + p(V_2 - V_1)$$

$$\Rightarrow \Delta_rH = \Delta_rU + p\Delta V \quad \dots(3.18)$$

Since for solids and liquids, ΔV , and hence $p\Delta V$ is negligible we can conclude that for reactions in solid and liquid phases,

$$\Delta_rH \approx \Delta_rU. \quad \dots(3.19)$$

However, in order to establish the relation for reactions involving gaseous reactants and/or products we need to make the following two assumptions

- all gaseous species (reactants and products) behave ideally and
- the total number of moles of gaseous reactants and products are n_1 and n_2 respectively

We can then write, using ideal gas equation,

$$p_1V_1 = n_1RT \quad \text{and} \quad p_2V_2 = n_2RT \quad \dots(3.20)$$

Since pressure is constant, we may write,

$$p(V_2 - V_1) = p\Delta V = (n_2 - n_1) RT \quad \dots(3.21)$$

$$\Rightarrow p\Delta V = \Delta n_g RT \quad \dots(3.22)$$

$$\text{where } \Delta n_g = (n_2 - n_1) = n_g(\text{products}) - n_g(\text{reactants}) \quad \dots(3.23)$$

Substituting in Eq. (3.18), we get

$$\Delta_r H = \Delta_r U + \Delta n_g RT \quad \dots(3.24)$$

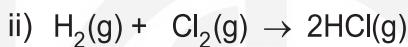
$$\Rightarrow \Delta_r U = \Delta_r H - \Delta n_g RT \quad \dots(3.25)$$

Let us take an example to understand the utility of this expression.

Example 3.2: Calculate the $\Delta_r U$ values for the chemical reactions given by following thermochemical equations at 298 K. What do you infer from the results obtained?



$$\Delta_r H = 483 \text{ kJ mol}^{-1}$$



$$\Delta_r H = -184.6 \text{ kJ mol}^{-1}$$



$$\Delta_r H = -114.6 \text{ kJ mol}^{-1}$$

Solution: Part (i): $\Delta n_g = n_g(\text{products}) - n_g(\text{reactants}) = 3 - 2 = 1$

We know: $\Delta_r U = \Delta_r H - \Delta n_g RT$

Substituting the values in Eq. (3.25),

$$\Delta_r U = 483.6 \text{ kJ mol}^{-1} - (1 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$= 483.6 \text{ kJ mol}^{-1} - 2.48 \text{ kJ mol}^{-1} = 481.12 \text{ kJ mol}^{-1}$$

Part (ii): $\Delta n_g = n_g(\text{products}) - n_g(\text{reactants}) = 2 - 2 = 0$

We know: $\Delta_r U = \Delta_r H - \Delta n_g RT$

Substituting the values in Eq. (3.25),

$$\Delta_r U = -184.6 \text{ kJ mol}^{-1} - (0 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$= -184.6 \text{ kJ mol}^{-1}$$

Part (iii): $\Delta n_g = n_g(\text{products}) - n_g(\text{reactants}) = 2 - 3 = -1$

We know: $\Delta_r U = \Delta_r H - \Delta n_g RT$

Substituting the values in Eq. (3.25),

$$\Delta_r U = -114.6 \text{ kJ mol}^{-1} - (-1 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

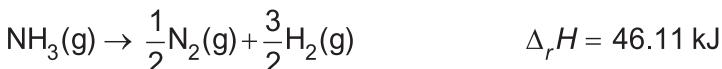
$$= -114.6 \text{ kJ mol}^{-1} + 2.48 \text{ kJ mol}^{-1} = -112.12 \text{ kJ mol}^{-1}$$

From the results obtained we can infer that if the number of moles of gaseous reactants and gaseous products are equal then, $\Delta_rH = \Delta_rU$ and if the number of moles of gaseous reactants are more than the number of moles of gaseous products then $\Delta_rH < \Delta_rU$. On the other hand if the number of moles of gaseous products are more than the number of moles of gaseous reactants then, $\Delta_rH > \Delta_rU$.

Having learnt about the energy changes accompanying chemical reactions and the related concepts, you may assess your understanding by solving the following self assessment questions.

SAQ 2

Calculate Δ_rU for the following reaction



SAQ 3

Complete the following thermochemical equation. (You may use suitable data from the example 2.2 given above)



3.3 STANDARD ENTHALPY OF FORMATION AND ITS DETERMINATION

You have learnt that every chemical reaction is associated with a specific value of the enthalpy change. As the total number of chemical reactions known is very large it would be inconvenient and impractical to determine and compile the enthalpy of reaction for all of them. The requirement of such a compilation can be avoided by finding and tabulating the standard enthalpies of formation of different chemical compounds. These can then be used to calculate the enthalpy changes associated with reactions. Let us learn about standard enthalpies of formation and their determination.

The standard or reference state of an element is, *its most stable state at the specified temperature and a pressure of 1 bar*.

The standard enthalpy of formation, Δ_fH° , of a compound is defined as the standard enthalpy of reaction for the formation of the compound from its elements in their standard states. The standard enthalpies of formation of elements in their standard states are zero by definition. For example, the enthalpy of formation of water in liquid state at 298.15 K can be represented as



Here, the superscript, $^\circ$ is indicative of the standard state and the subscript; f represents 'formation'. The expression implies that one mole of hydrogen gas

reacts with half a mole of oxygen gas to give one mole of liquid water in their standard states at 298.15 K and 1 bar. Similarly, for carbon dioxide gas at 298.15 K we can write,



The standard enthalpy of formation of some of the compounds is given in Table 3.1.

Table 3.1: Standard molar enthalpies (in kJ mol^{-1}) of formation for some common compounds

Compound	Standard molar enthalpy / kJ mol^{-1}	Compound	Standard molar enthalpy / kJ mol^{-1}
CO(g)	-110.5	HBr(g)	-36.40
CO ₂ (g)	-393.5	HI(g)	26.48
CH ₄ (g)	-74.81	H ₂ O(g)	-241.8
C ₂ H ₂ (g)	226.7	H ₂ O(l)	-285.8
C ₂ H ₄ (g)	52.26	H ₂ S(g)	-20.63
C ₂ H ₆ (g)	-84.68	NH ₃ (g)	-46.11
C ₃ H ₈ (g)	-103.8	NO(g)	90.25
C ₄ H ₁₀ (g)	-125.6	N ₂ O(g)	82.05
CH ₃ OH(l)	-238.7	NO ₂ (g)	33.18
C ₂ H ₅ OH(l)	-277.7	N ₂ O ₄ (g)	9.16
HF(g)	-271.1	SO ₂ (g)	-296.8
HCl(g)	-92.31	SO ₃ (g)	-395.7
HCHO(g)	-117.00	CH ₃ CHO (l)	-192.30

3.3.1 Enthalpy of Formation and Enthalpy of Reaction

An important consequence of defining the enthalpy of formation is that the enthalpy of a reaction can be expressed in terms of the difference in the enthalpies of formation of the products minus those of the reactants. Let us reconsider the formation of carbon dioxide from C (graphite) and oxygen as given below.



Let us represent the enthalpy of the reaction in terms of the enthalpy of formation of the products and reactants as given below.

$$\Delta_r H^0 = \Delta_f H^0(\text{CO}_2) - \Delta_f H^0(\text{O}_2) - \Delta_f H^0(\text{C, graphite}) \quad \dots (3.29)$$

Since the enthalpies of formation for the elemental oxygen and carbon are zero by definition, we get

$$\Delta_r H^0 = \Delta_f H^0(\text{CO}_2) - 0 - 0 = \Delta_f H^0(\text{CO}_2) \quad \dots (3.30)$$

This equation is quite important as it allows us to calculate the enthalpy change for any reaction whether feasible or not.

This fact can be generalised and we can write that

$$\Delta_r H^\circ = \sum_{\text{Products}} v \Delta_f H^\circ - \sum_{\text{Reactants}} v \Delta_f H^\circ \quad \dots (3.31)$$

Where, v refers to the stoichiometric coefficients for the reactants and products in the balanced chemical equation. Let us take an example to calculate the enthalpy of a reaction using Eq. 3.31.

Example 3.3: The combustion of methane is given by the following expression.



Calculate the enthalpy of the combustion of methane in terms of enthalpies of formation of the reactants and the products. Use data from Table 3.1.

Solution: As per Eq.(3.31) the enthalpy of the combustion of methane, can be written as

$$\Delta_r H^\circ = \Delta_f H^\circ (\text{CO}_2(\text{g})) + 2\Delta_f H^\circ (\text{H}_2\text{O}(\text{l})) - \Delta_f H^\circ (\text{CH}_4(\text{g})) - 2\Delta_f H^\circ (\text{O}_2(\text{g}))$$

Substituting the values from the Table 3.1, we get,

$$\begin{aligned}\Delta_r H^\circ &= -393.5 - (2 \times 285.8) - (-74.74) - 0.0 \\ &= -890.36 \text{ kJ mol}^{-1}\end{aligned}$$

Thus, you can note that Eq. (3.31) is quite useful in calculating the enthalpies of reactions. Let us learn about the methods for the determination of standard enthalpies of formation. However, before that answer the following SAQ

SAQ 4

The thermochemical equation for the combustion of benzene is given below,



Calculate the enthalpy of formation of benzene. (You may use the data from Table 3.1 as required).

3.3.2 Direct Determination of Enthalpy of Formation

The direct determination of the standard enthalpies of formation $\Delta_f H^\circ$ is possible only for those compounds that can be readily synthesized from their elements. In such cases the formation of a compound from its elements is carried out in a calorimeter and the enthalpy change for the reaction is directly measured. For example, the enthalpy of formation of carbon dioxide can be readily determined by measuring the enthalpy of the reaction between carbon (graphite) and molecular oxygen in their standard states to give carbon dioxide in its standard state as given by the following equation.



Similarly, measuring the enthalpy of reaction between sulphur and fluorine in their standard states can provide the standard enthalpy of formation of SF_6 as given below.



You may note here that the rhombic form is the standard state of elemental sulphur. Though this method of determination of standard enthalpy of formation is quite straight forward, it is generally not used because there are not many compounds that can directly prepared from their elements in the standard state. In such cases, $\Delta_f H^\circ$ is determined by an indirect method based on Hess's law of constant heat summation. Let us learn about the indirect method

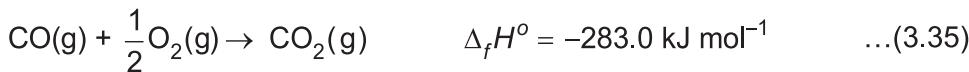
3.3.3 Indirect Determination of Enthalpy of Formation

The indirect method for the determination of the enthalpy of formation is based on an important empirical law of thermochemistry discovered by G. H. Hess in 1840. The law states that, “the enthalpy change associated with a given chemical reaction is the same whether it occurs in a single stage or in many stages”. The law is commonly known as the law of constant heat summation and implies that the net enthalpy change for a reaction depends only on the initial and final states, and not on the intermediate states through which the system passes. An important consequence of the Hess's law is that the thermochemical equations can be added and subtracted, like algebraic equations. Let us take an example,

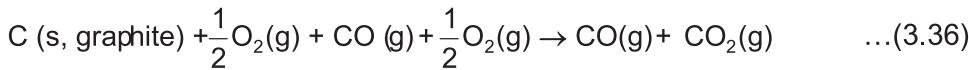
The partial oxidation of graphite to carbon monoxide can be represented by the following thermochemical equation,



and the oxidation of carbon monoxide to carbon dioxide is given as



Let us add these two equations Eq. (3.35) and Eq. (3.36), to get



The corresponding enthalpies add as

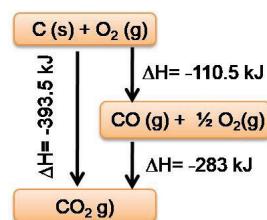
$$\Delta_f H^\circ = (-110.5 \text{ kJ mol}^{-1}) + (-283.0 \text{ kJ mol}^{-1}) = -393.5 \text{ kJ mol}^{-1} \quad \dots(3.37)$$

The resulting thermochemical equation can be written as



This equation is the same as Eq.(3.32), representing the formation of CO_2 from its elements in the standard states.

The Hess's law of constant heat summation follows directly from the first law of thermodynamics. We know that enthalpy, H is a state function and ΔH depends only on the initial and final state (that is, only on the nature of reactants and the products).



This consequence of the Hess's law forms the basis for the indirect determination of the enthalpies of formation. In order to apply Hess's law the first step is to identify a set of chemical reactions such that their equations can be arranged in such a way that, when added together, all species other than the reactants and products of the desired reaction cancel out. This may involve multiplying certain equations with suitable coefficients or reversing some reactions.

3.4 ENTHALPY CHANGES IN DIFFERENT TYPES OF REACTIONS

The enthalpies of some of the types of reactions have been assigned special names and are quite important. Let us learn about these enthalpies.

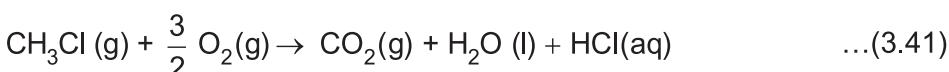
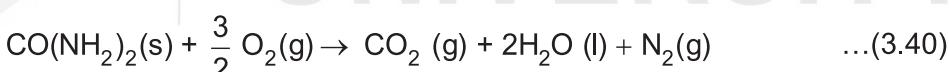
3.4.1 Enthalpy Changes in Combustion Reaction

You may note here that the reactants and the products are in their standard states.

As you are aware, combustion refers to the reaction of a compound with an oxidant (usually oxygen) to produce oxidized products accompanied by energy. The standard enthalpy of combustion of a compound is defined as the enthalpy change accompanying the complete combustion of one mole of the compound in presence of sufficient oxygen under standard conditions. All the reactants and the products are in their standard states. For example the combustion of carbon and ethanol are represented as:



The products of combustion for the compounds containing C, H and O are carbon dioxide in the gaseous state and water in the liquid state. In case the compound also contains N, the nitrogen gas is obtained in the products and the compounds containing halogens produce aqueous solutions of halogen acids at infinite dilution.



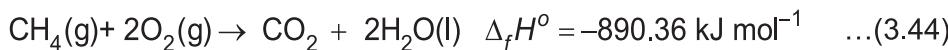
One of the applications of the values of the enthalpies of combustion is in the determination of the standard enthalpy of formation of compounds, which cannot be measured directly. Let us take an example to learn how do we use enthalpy of combustion to get standard enthalpy of formation? We make use of the Hess's law for this purpose.

Example 3.4: Determine the enthalpy of formation of methane from its elements using Hess's law.

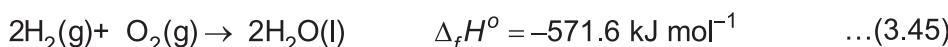
Solution: You know that the enthalpy of formation of methane corresponds to the enthalpy change for the following reaction



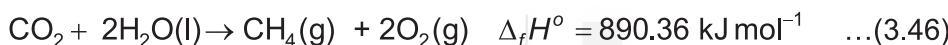
You would recall from above that the direct determination of enthalpy of formation of methane is not possible. We identify the following equations involving the combustion of the reactants and the products



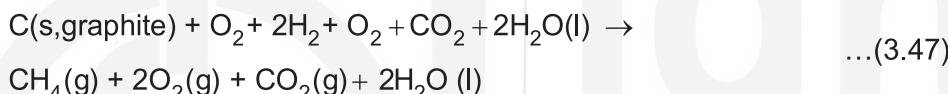
The formation reaction involves one mole of carbon and two moles of hydrogen therefore we multiply Eq. (3.43) by two to get



Further, as we need to get one mole of methane as the product we reverse Eq.3.44 i.e.,



Now adding, Eq. (3.32), (3.45) and (3.46) we get,



Cancelling the common terms on the two sides we get, the desired expression for the formation of methane,



The corresponding enthalpy change can be calculated as

$$\Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1} - 571.6 + 890.36 = -74.74 \text{ kJ mol}^{-1}$$

You must recall from above that when a thermochemical equation is multiplied by a number 'n' then the enthalpy change, ΔH , for the reaction must also change by the same factor and secondly, if we reverse the equation, then the sign of enthalpy change also changes and the magnitude remains the same.

3.4.2 Enthalpy Changes in Dissolution and Dilution

The enthalpy of dissolution refers to the enthalpy change accompanying the dissolution of a solute in a solvent or the process of solution formation. The enthalpy of solution formation depends on the composition of solution besides the nature of solute and solvent. In the context of composition of solution, we define **integral enthalpy of solution**, as *the enthalpy change associated with the addition of a specified amount of solute to a specified amount of solvent under standard conditions*. For example, the following thermochemical equation,



represents the dissolution of 1 mole of HCl in 5 moles of water. Here, 'HCl.5aq' represents a solution of 1 mole of HCl in 5 moles of H₂O. In other words, the enthalpy change accompanying the process (Eq. 3.48) is called integral enthalpy of solution for the dissolution of 1 mole of HCl in 5 moles of water. The integral enthalpy of solution depends on the molar ratio of the solute and the solvent as shown in the following equations.

$\text{HCl (g)} + 10 \text{ aq} \rightarrow \text{HCl.10aq}$	$\Delta H = -69.01 \text{ kJ mol}^{-1}$...(3.49)
$\text{HCl (g)} + 25 \text{ aq} \rightarrow \text{HCl.25aq}$	$\Delta H = -72.03 \text{ kJ mol}^{-1}$...(3.50)
$\text{HCl (g)} + 40 \text{ aq} \rightarrow \text{HCl.40aq}$	$\Delta H = -72.79 \text{ kJ mol}^{-1}$...(3.51)
$\text{HCl (g)} + 100 \text{ aq} \rightarrow \text{HCl.100aq}$	$\Delta H = -73.61 \text{ kJ mol}^{-1}$...(3.52)
$\text{HCl (g)} + 200 \text{ aq} \rightarrow \text{HCl.200 aq}$	$\Delta H = -73.96 \text{ kJ mol}^{-1}$...(3.53)
$\text{HCl (g)} + \infty \text{ aq} \rightarrow \text{HCl.}\infty\text{ aq}$	$\Delta H = -74.85 \text{ kJ mol}^{-1}$...(3.54)

Thus, the integral enthalpy of solution can be seen as the enthalpy change accompanying the dissolution of 1 mole of the solute in a definite quantity of solvent to get a solution of the desired concentration. A look at the Eq. (3.49) to Eq. (3.54) shows that as we add more and more solvent to a given amount of the solute the integral enthalpy of solution reaches a limiting value. This limiting value is called the **integral enthalpy of solution at infinite dilution**, $\Delta_{\infty}H^{\circ}$. Any further addition of solvent does not alter the enthalpy change value.

We may take a solution of known concentration (solute-solvent ratio) and add a definite amount of solvent to get a solution of a lower concentration. This process is called dilution and the enthalpy change accompanying this process is called **enthalpy of dilution**. Let us take an example wherein a solution of HCl(g) in water having solute-solvent mole ratio of 1:10 and we add 15 moles of water to it. The process will be represented as



The enthalpy change for this process can be obtained with the help of Hess's law. Let us rewrite Eq.(3.49) and Eq. (3.50),



Subtracting Eq. (3.49) from Eq.(3.50) and rearranging we get the reaction given in Eq. (3.55) and the associated enthalpy change.



Thus, we can define the enthalpy of dilution as the enthalpy change accompanying the dilution of a solution containing 1 mole of solute from a given concentration to a lower concentration.

SAQ 5

An aqueous solution of HCl in water having solute-solvent mole ratio of 1:25, is diluted by adding sufficient solvent such that any further addition of solvent does not change its enthalpy. Represent the process in the form of an equation and compute the enthalpy change for the process. [You may use data from Eq.(3.49) to Eq. (3.54) as required].

3.5 TEMPERATURE DEPENDENCE OF Δ_rH : KIRCHHOFF'S EQUATION

You have learnt that the enthalpy of different types of reactions can be computed with the help of enthalpy of formation of different compounds. However, most of the data available on enthalpy of reaction or enthalpy of formation of compounds are at 298 K. If the enthalpy of reaction is required at some other temperature, we need to know the temperature dependence of the enthalpy of reaction. The enthalpy of reaction at a desired temperature can be obtained from the enthalpy of reaction at some other temperature with the help of Kirchhoff's equation. Let us derive Kirchhoff's equation.

We know that: $\Delta_rH^\circ = H^\circ(\text{products}) - H^\circ(\text{reactants})$

Differentiating with respect to temperature we get,

$$\frac{d}{dT}(\Delta_rH^\circ) = \frac{d}{dT}H^\circ(\text{products}) - \frac{d}{dT}H^\circ(\text{reactants}) \quad \dots(3.57)$$

As $\frac{d}{dT}H^\circ = C_p^\circ$ we can write

$$\frac{d}{dT}(\Delta_rH^\circ) = C_p^\circ(\text{products}) - C_p^\circ(\text{reactants}) \quad \dots(3.58)$$

$$\frac{d}{dT}(\Delta_rH^\circ) = \Delta C_p^\circ \quad \dots(3.59)$$

Writing the equation in the differential form

$$d(\Delta_rH^\circ) = \Delta C_p^\circ dT \quad \dots(3.60)$$

Integrating the equation between temperatures T_1 and T_2 ,

$$\int_{T_1}^{T_2} d(\Delta_rH^\circ) = \int_{T_1}^{T_2} \Delta C_p^\circ dT \quad \dots(3.61)$$

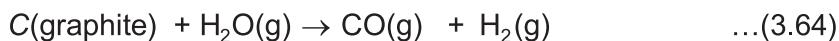
$$\Delta_rH^\circ(T_2) - \Delta_rH^\circ(T_1) + \Delta C_p^\circ (T_2 - T_1) \quad \dots(3.62)$$

Rearranging,

$$\Delta_rH^\circ(T_2) = \Delta_rH^\circ(T_1) + \Delta C_p^\circ (T_2 - T_1) \quad \dots(3.63)$$

This is the Kirchhoff's equation that gives the temperature dependence of enthalpy change for a reaction. Let us take up an example to learn about the application of Kirchhoff's equation.

Example 3.5: The enthalpy change for the following reaction is determined to be $131.28 \text{ kJ mol}^{-1}$ at 298 K.



Calculate the enthalpy change for the reaction at 100°C . The C_p° ($\text{J K}^{-1} \text{mol}^{-1}$) values are given as: C (graphite) = 8.53; $\text{H}_2\text{O(g)}$ = 33.58; CO (g) = 29.12; $\text{H}_2\text{(g)}$ = 28.82. Assume the heat capacity values to be temperature independent in the range.

Solution: As per Eq. (3.63):

$$\Delta H^\circ(T_2) = H^\circ(T_1) + \Delta C_p^\circ (T_2 - T_1)$$

We begin by calculating the C_p° values

$$\Delta C_p^\circ = C_p^\circ[\text{CO(g)}] + C_p^\circ[\text{H}_2\text{(g)}] - C_p^\circ[\text{C(graphite)}] - C_p^\circ[\text{H}_2\text{O(g)}] \quad \dots(3.59)$$

Substituting the values

$$\Delta C_p^\circ = 29.12 + 28.82 - 8.53 - 33.58 = 15.83 \text{ J K}^{-1} \text{ mol}^{-1}$$

Substituting in Eq. (3.63)

$$\Delta H^\circ(373.15) = 131.28 \text{ kJ mol}^{-1} + 15.83 \text{ J K}^{-1} (373.15 - 298) \text{ K}$$

Solving, we get, $\Delta H^\circ(373.15) = 130.09 \text{ kJ mol}^{-1}$

3.6 BOND ENTHALPIES AND ESTIMATION OF ENTHALPIES OF REACTION

You know that a chemical reaction involves breaking and making of bonds. We may ask, "Can we determine the enthalpy of a reaction in terms of bond enthalpies?". The answer is yes, let us learn about the meaning of bond enthalpies and how can these be used to determine the enthalpy of reaction.

3.6.1 Bond Enthalpies

Let us consider the following thermochemical reactions

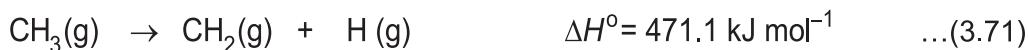


The enthalpy changes in these reactions indicate the amount of energy required to break the covalent bonds in 1 mole of the respective gaseous diatomic molecules. These numbers are in fact a measure of the strengths of the bonds. These energies are called **bond enthalpies** and are directly measurable in case of homonuclear diatomic molecules. The bond enthalpies for heteronuclear diatomic molecules can also be directly measured. For example,



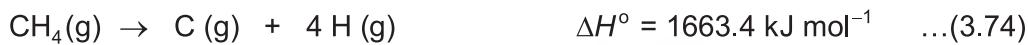
However, for larger molecules the same is not true. Let us take the successive dissociation of C-H bonds in methane.

The bond enthalpies for diatomic (homonuclear and heteronuclear) molecules simply are the bond dissociation energies and are directly measurable.



You can observe here that each of these equations represent the dissociation of a C-H bond but the energies required for them are different. Though all the C-H bonds in methane are equivalent the dissociation energies are not the same. This is due to the fact that once a C-H bond is dissociated; the remaining species has different electronic distributions.

We can add these four equations to get,



In this reaction the methane molecule has got converted into its constituent atoms therefore the enthalpy change is called the enthalpy of atomization of methane. If we divide the enthalpy of atomization of methane by 4 (the number of C-H bonds broken), we get an average value ($1663.4 / 4 = 415.9 \text{ kJ mol}^{-1}$) for the bond enthalpy for C-H bond.

Similarly, we can take up the case of the dissociation of O-H bonds in water.



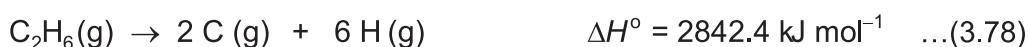
Adding the two, we get



Here again the two bond dissociation energies are different and their average value ($464.5 \text{ kJ mol}^{-1}$) is the bond enthalpy for the O-H bond. Another example could be the dissociation of N-H bonds of ammonia. In all these molecules we have equivalent bonds.

If we extend the argument further and try to determine the bond enthalpy for the molecule like ethane. In such a case two different types of bonds exist, e.g., C-H and C-C bonds. In order to determine bond enthalpies we need to introduce some assumption, as we cannot get the value of two unknowns from one data (i.e., enthalpy of atomization of ethane).

We assume that the bond enthalpy for a given bond (say C-H) in ethane is same as that in methane. The atomization of ethane is given by the following expression.



The enthalpy of atomization of ethane would equal the bond enthalpies of six C-H bonds and one C-C bond. If we subtract the bond enthalpies of six C-H bonds from the enthalpy of atomization we can get the bond enthalpy for C-C bond. Thus, the bond enthalpy for a given bond refers to the average bond dissociation energy for the same bond in a number of related molecules having the said bond. This way the bond enthalpies for different bonds are determined and are compiled. Table 3.2 gives the bond enthalpies of different types of bonds.

Table 3.2: Bond Enthalpies of Common Bonds

Bond	Bond Enthalpy (kJ mol ⁻¹)	Bond	Bond Enthalpy (kJ mol ⁻¹)
H—H	436.4	C—S	255
H—N	393	C = S	477
H—O	460	N—N	193
H—S	368	N = N	418
H—P	326	N ≡ N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N = O	607
H—Br	366.1	O—O	142
H—I	298.3	O = O	498.7
C—H	415.9	O—P	502
C—C	347	O = S	469
C = C	620	P—P	197
C ≡ C	812	P = P	489
C—N	276	S—S	268
C = N	615	S = S	352
C ≡ N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C = O [†]	745	Br—Br	192.5
C—P	263	I—I	151.0
C—Br	234		

3.6.2 Enthalpy of Reaction from Bond Enthalpies

As you know that any chemical reaction can be seen in terms of breaking and making of chemical bonds. That is we need energy to break chemical bonds and formation of new chemical bonds is accompanied by a release of energy. Therefore, it is possible to predict the approximate enthalpy of reaction by using the average bond enthalpies. This is done by counting the number of

bonds being broken and the new bonds being formed in the reaction and accounting for the energy changes involved. The enthalpy of reaction in the gas phase is given simply by the following expression.

$$\Delta H^\circ = \text{Total energy input} - \text{total energy output} \quad \dots(3.79)$$

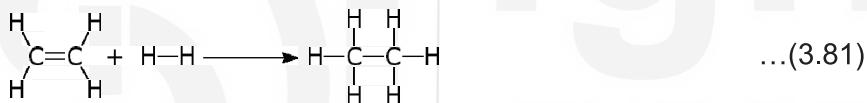
As the energy input is to break the bonds and energy output is in the process of bond making, we can write

$$\Delta_r H^\circ = \sum \text{Bond Enthalpy (Reactants)} - \sum \text{Bond Enthalpy (Products)} \quad \dots(3.80)$$

If the sum of bond enthalpies of all the reactants (energy input) is greater than the sum of bond enthalpies of all the products (energy output), ΔH° is positive and the reaction is endothermic. On the other hand, if the reverse is true, ΔH° is negative and the reaction is exothermic. Let us take an example to understand the determination of enthalpy of a reaction using bond enthalpies.

Example 3.6: Predict the enthalpy of hydrogenation of ethene to ethane using the bond enthalpy data from Table 3.2. Compare it with the same calculated on the basis of standard enthalpy of formation values from Table 3.1.

Solution: The hydrogenation of ethene is given by the following equation.



As explained above, to calculate the enthalpy of the reaction we first need to list the bonds being broken and the bonds being formed.

The bonds being broken: 1 C=C, 4 C-H and 1 H-H

The bonds being formed: 1 C-C and 6 C-H

The energy spent on breaking the bonds, Σ Bond Enthalpy (Reactants)

Substituting the values from Table 3.2,

$$= 1 (620 \text{ kJ mol}^{-1}) + 4 (415.9 \text{ kJ mol}^{-1}) + 1 (436.4 \text{ kJ mol}^{-1}) = 2720 \text{ kJ mol}^{-1}$$

The energy released in formation the bonds, Σ Bond Enthalpy (Products)

Substituting the values from Table 3.2,

$$= 1 (347 \text{ kJ mol}^{-1}) + 6 (415.9 \text{ kJ mol}^{-1}) = 2842.4 \text{ kJ mol}^{-1}$$

The enthalpy of reaction:

$$\Delta_r H^\circ = \Sigma \text{ Bond Enthalpy (Reactants)} - \Sigma \text{ Bond Enthalpy (Products)}$$

Substituting the values from Table 3.1

$$\Delta_r H^\circ = 2720 - 2842.4 = -122.4 \text{ kJ mol}^{-1}$$

Thus, the enthalpy of hydrogenation of ethene as calculated above on the basis of bond enthalpies is found to be = $-122.4 \text{ kJ mol}^{-1}$.

Let us calculate the same by using the standard enthalpies of formation of the reactants and the products. For the given reaction we can write,

$$\Delta_r H^0 = \Delta_f H^0(\text{C}_2\text{H}_6) - \Delta_f H^0(\text{C}_2\text{H}_4) - \Delta_f H^0(\text{H}_2) \quad \dots(3.82)$$

Substituting the values from Table 3.1,

$$\Delta_r H^0 = -84.68 - 52.26 - 0 = -136.94 \text{ kJ mol}^{-1}$$

The discrepancy in the two values is due to the fact that some of the bond enthalpies used are average values.

Why don't you practice the method for calculation of enthalpy of reaction from bond enthalpies by solving the following SAQ

SAQ 6

Predict the enthalpy change for the addition of HBr to ethene on the basis of bond enthalpies. Use Table 3.2

3.7 SUMMARY

In this unit we continued our discussion on the applications of the first law of thermodynamics and focused on thermochemistry—the study of the heat changes associated with chemical reactions. We began by discussing the energy changes accompanying chemical reactions under the conditions of constant volume and constant pressure and learnt about their experimental determination by calorimetry. Since vast majority of the chemical reactions are performed under the conditions of constant pressure, we introduced the concept of enthalpy of reaction as the heat change accompanying a chemical reaction. It was shown that the enthalpy change for a reaction equals the sum of enthalpies of the products minus the sum of enthalpies of the reactants.

In order to highlight the energy changes accompanying the chemical reaction, the concept of thermochemical equations was introduced. In thermochemical equations the energy changes are integrated with the chemical equation. The meaning of thermochemical equations was explained and their characteristics and significance was discussed. As the enthalpy change for a reaction depends on variety of parameters like, pressure, temperature, concentration, and the physical state of the reactants and the products, etc. we argued for and defined standard enthalpy change. This refers to the enthalpy change associated with a reaction in which the reactants and the products are in their standard states. This in turn necessitated the need for a standard state, which was defined.

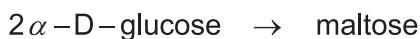
We then defined the standard enthalpy of formation as the enthalpy of reaction for the formation of the compound from its elements in their standard or reference states. The importance of standard enthalpies of formation was

demonstrated in terms of their ability to give enthalpy of a reaction. The enthalpy of reaction is equal to the difference in the sum of enthalpies of formation of the products minus the sum of enthalpies of formation of the reactants. Owing to their importance we discussed about the direct and indirect determination of the enthalpies of formation of compounds. In the context of indirect determination, we introduced a very important empirical law, called Hess's law of constant heat summation and discussed about its importance and applications.

Then we took up the enthalpy changes associated with different types of chemical reactions. Herein we defined standard enthalpies of combustion, dissolution and dilution. We demonstrated how we could use enthalpies of combustion for the determination of enthalpies of formation of compounds. Since temperature is one of the important variables in thermodynamics; we took up the variation in the enthalpy changes with temperature. In this context we formulated the Kirchhoff's equation and discussed its importance. We showed with the help of examples that if we know the enthalpy of reaction at a given temperature, the same at some other temperature can be calculated if we know the heat capacities of the reactants and the products. Towards the end of the unit we introduced the concept of bond enthalpy and demonstrated how the bond enthalpies can be used to predict enthalpy of reaction.

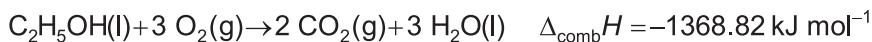
3.8 TERMINAL QUESTIONS

1. Why is the bomb calorimeter so called?
2. Enlist salient features of thermochemical equations.
3. What is meant by standard state? Why do we need to define standard state?
4. Two molecules of α -D-glucose condense in an enzyme catalysed reaction to give a molecule of disaccharide, maltose. The reaction is as under



Calculate the enthalpy of the reaction. The enthalpies of combustion for crystalline α -D-glucose and maltose at 298 K are $-2809.1 \text{ kJ mol}^{-1}$ and $-5645.5 \text{ kJ mol}^{-1}$ respectively.

5. The thermochemical equation for the combustion of ethanol is given below,



Calculate the enthalpy of formation of ethanol. (You may use the data from Table 3.2 as required)

6. The standard enthalpy of formation of $\text{NO}_2\text{(g)}$ is found to be $-33.18 \text{ kJ mol}^{-1}$. Calculate the enthalpy of formation of NO_2 at 100°C .
The C_p values are:

$O_2(g) = 29.36$; $NO_2(g) = 37.20$; $N_2(g) = 29.13$. Assume the heat capacity values to be temperature independent in the range of the temperature.

3.9 ANSWERS

Self-Assessment Questions

1. As per the Eq. (3.1) and (3.2) we can write,

$$q_{\text{rexn.}} = -C_{\text{calorimeter}} \Delta T$$

$$\text{Given: } \Delta T = 3.9 \text{ K} \quad C_{\text{calorimeter}} = 9.4 \text{ k J K}^{-1}$$

Substituting the values in the equation,

$$q_{\text{rexn.}} = -9.4 \text{ kJ K}^{-1} \times 3.9 \text{ K} = -36.66 \text{ kJ}$$

Thus, the combustion of 1.75 g of ethanol with an excess of oxygen is associated with the release of 36.66 kJ of energy as heat. In order to obtain the heat change expected for 1 mole of ethanol we calculate the change per gram and then per mole as given below.

Heat change per g of ethanol

$$q_{\text{rexn.}} = \frac{-36.66 \text{ kJ}}{1.75 \text{ g}} = -20.95 \text{ kJ g}^{-1}$$

Heat change per mole of ethanol =

$$q_{\text{rexn.}} = -20.95 \text{ kJ g}^{-1} \times 46 \text{ gmol}^{-1} = -963.7 \text{ kJ mol}^{-1}$$

2. $\Delta n_g = n_g(\text{products}) - n_g(\text{reactants}) = 2 - 1 = 1$

We know: $\Delta_r U = \Delta_r H - \Delta n_g RT$

Substituting the values,

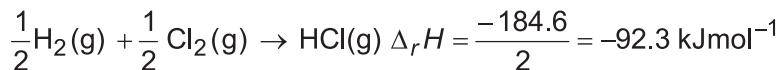
$$\Delta_r U = 46.11 \text{ kJ mol}^{-1} - (1 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K})$$

$$= 46.11 \text{ kJ mol}^{-1} - 2.48 \text{ kJ mol}^{-1} = 43.63 \text{ kJ mol}^{-1}$$

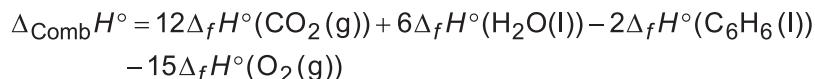
3. As per example 3.3,



The given expression can be obtained by dividing this equation by 2 therefore the enthalpy change also would be half of the value in the example. That is we can write,



4. As per Eq.(3.28) the enthalpy of the combustion for the given reaction can be written as



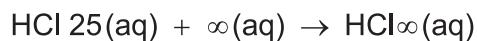
Substituting the values from the Table 3.1, we get,

$$-(12 \times 393.5) - (6 \times 285.8) - 2\Delta_f H^\circ(C_6H_6(l)) - 0.0 = -6535 \text{ kJ mol}^{-1}$$

$$\text{Solving, } -2\Delta_f H^\circ(C_6H_6(l)) = -98.2 \text{ kJ mol}^{-1}$$

$$\Rightarrow \Delta_f H^\circ(C_6H_6(l)) = -49.1 \text{ kJ mol}^{-1}$$

5. The process can be represented by the following equation,



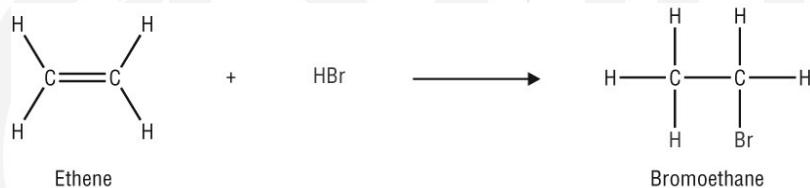
In order to calculate the enthalpy change for the process we use the thermochemical Eq. (3.50) and Eq. (3.54)



Subtracting Eq. (3.50) from Eq. (3.54) we get



6. The reaction can be represented as



In order calculate the enthalpy of the reaction we first need to list the bonds being broken and the bonds being formed.

The bonds being broken: 1 C=C, 4 C-H and 1 H-Br

The bonds being made: 1 C-C , 5 C-H and 1 C-Br

The energy spent on breaking the bonds, Σ Bond Enthalpy (Reactants)

$$= 1 (620 \text{ kJ mol}^{-1}) + 4 (415.9 \text{ kJ mol}^{-1}) + 1 (366.1 \text{ kJ mol}^{-1})$$

$$= 2649.7 \text{ kJ mol}^{-1}$$

The energy released on making the bonds, Σ Bond Enthalpy (Products)

$$= 1 (347 \text{ kJ mol}^{-1}) + 5 (415.9 \text{ kJ mol}^{-1}) + 1 (234)$$

$$= 2660 \text{ kJ mol}^{-1}$$

The enthalpy of reaction:

$$\Delta_r H^\circ = \Sigma \text{Bond Enthalpy (Reactants)} - \Sigma \text{Bond Enthalpy (Products)}$$

Substituting the values,

$$\Delta_r H^\circ = 2649.17 - 2660.5 = -10.8 \text{ kJ mol}^{-1}$$

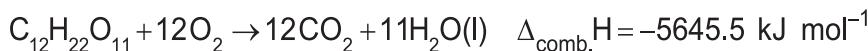
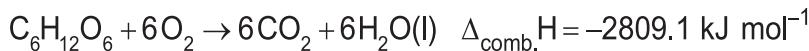
Thus, the enthalpy of addition of HBr to ethene as calculated above on the basis of bond enthalpies is found to be = $-10.8 \text{ kJ mol}^{-1}$.

Terminal Questions

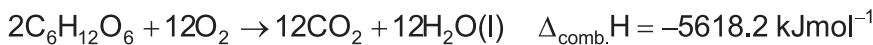
1. In constant volume calorimetry a known quantity of the reactant and oxygen gas under pressure is placed in the container and combusted with the help of an electrical ignition. The reaction is accompanied with a minor explosion. It is because of this the reaction vessel is called a bomb.
2. A thermochemical equation is an equation that is a combination of the chemical equation and the associated enthalpy change. It consists of the chemical formulae of the reactants and the products along with their stoichiometric coefficients, physical state and enthalpy change.

The salient features of the thermochemical equations are as under:

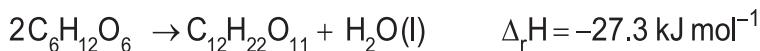
- The enthalpy change refers to the reaction as written i.e., it corresponds to one mole of the reaction. If a thermochemical equation is multiplied by a factor 'n' on both sides, then the enthalpy change, $\Delta_r H$, for the reaction must also change by the same factor.
 - It is mandatory to specify the state of the reactants and the products in the thermochemical equation
 - In case the chemical equation is reversed, the sign of enthalpy change would change; magnitude remaining the same.
3. The standard state of a substance at a specified temperature is defined as its pure form at a pressure of 1 bar. We need to define a standard state so as to be able to define the standard enthalpy change, which is the enthalpy change for a reaction in which the reactants and products are in their standard states. This facilitates the compilation and comparison of the enthalpy change data.
 4. On the basis of given data we can write the following thermochemical equations:



Multiply Eq.1 by 2



Subtracting Eq.2 from the above equation, we get



5. On the basis of given thermochemical equation we can write,

$$\Delta_{\text{comb.}}H^{\circ} = -1368.82 \text{ kJ mol}^{-1}$$

$$= 3\Delta_f H^{\circ}(\text{H}_2\text{O(l)}) + 2\Delta_f H^{\circ}(\text{CO}_2\text{(g)}) - \Delta_f H^{\circ}(\text{C}_2\text{H}_5\text{OH(l)}) - 3\Delta_f H^{\circ}(\text{O}_2\text{(g)})$$

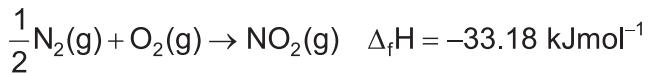
Substituting the values,

$$-1368.82 \text{ kJ mol}^{-1} = 3(-285.8) + 2(-393.5) - \Delta_f H^{\circ}(\text{C}_2\text{H}_5\text{OH(l)}) - 3(0.0)$$

Solving we get

$$\Delta_f H^{\circ}(\text{C}_2\text{H}_5\text{OH(l)}) = -275.58 \text{ kJ mol}^{-1}$$

6. The formation of NO_2 can be given as



As per Eq. (3.63): $\Delta_r H^{\circ}(T_2) = \Delta_r H^{\circ}(T_1) + \Delta C_p^{\circ} (T_2 - T_1)$

We begin by calculating the ΔC_p° values

$$\Delta C_p^{\circ} = C_p^{\circ}[\text{NO}_2\text{(g)}] - C_p^{\circ}[\text{O}_2\text{(g)}] - \frac{1}{2}C_p^{\circ}[\text{N}_2\text{(g)}]$$

Substituting the values

$$\Delta C_p^{\circ} = 37.20 - 29.36 - \frac{1}{2}(29.13) \text{ JK}^{-1}\text{mol}^{-1}$$

Solving

$$\Delta C_p^{\circ} = 6.725 \text{ JK}^{-1}\text{mol}^{-1}$$

Substituting in Eq. (3.63)

$$\Delta H^{\circ}(373.15) = -33.18 \text{ kJ mol}^{-1} - 6.725 \text{ JK}^{-1}(373.15 - 298) \text{ K}$$

Solving, we get

$$\Delta H^{\circ}(373.15) = -33.685 \text{ kJ mol}^{-1}$$